SUPPORTING INFORMATION FOR:

Closing the loop in the synthesis of heteroscorpionate-based aluminium helicates. Catalytic studies for cyclic carbonate synthesis.

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Figure S1. Tautomers of acetamide or thioacetamide heteroscorpionate ligands

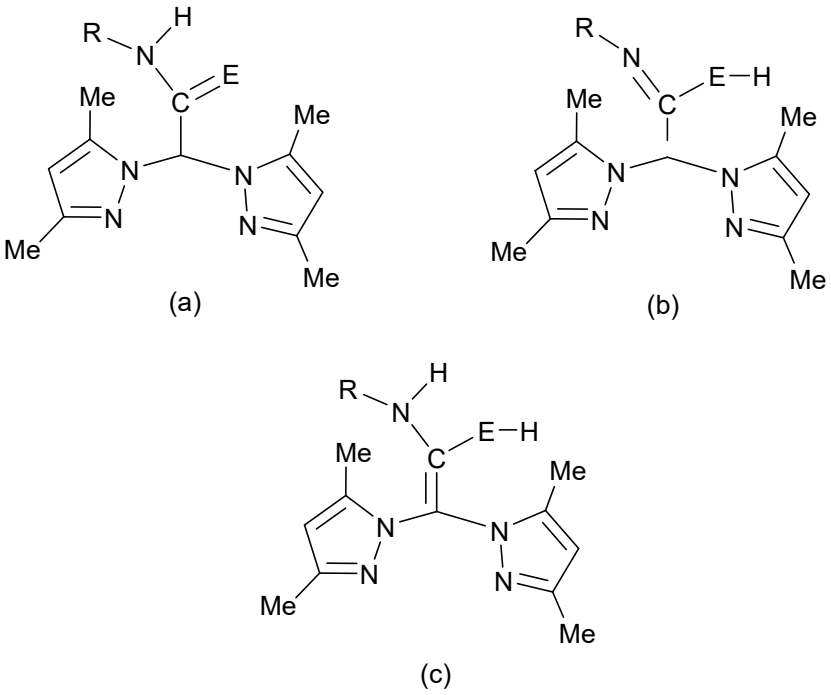


Figure S2. Variable temperature ^{1}H NMR spectra in the region from 6.0 to 3.5 ppm for compound **9** in toluene-d_8

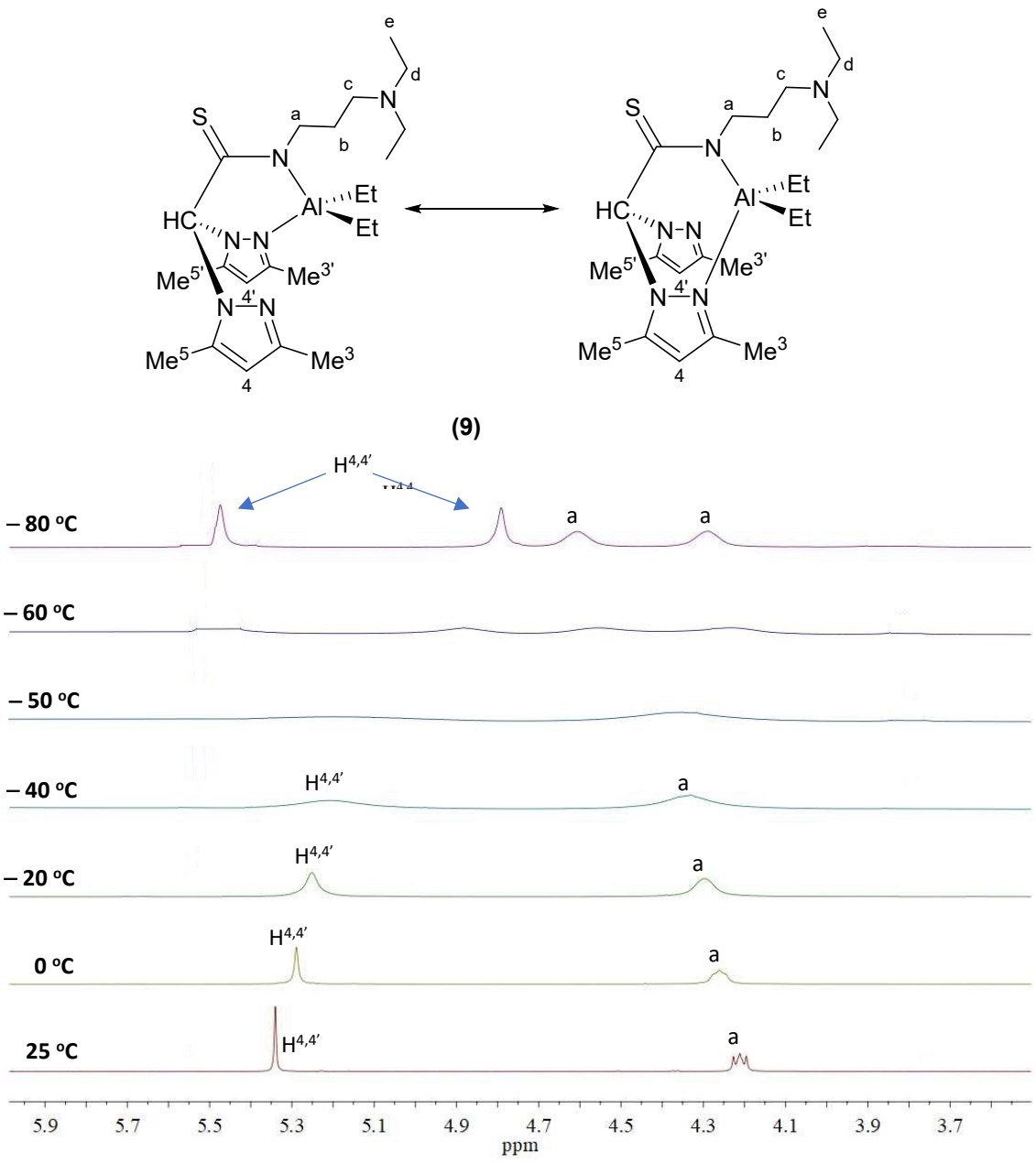
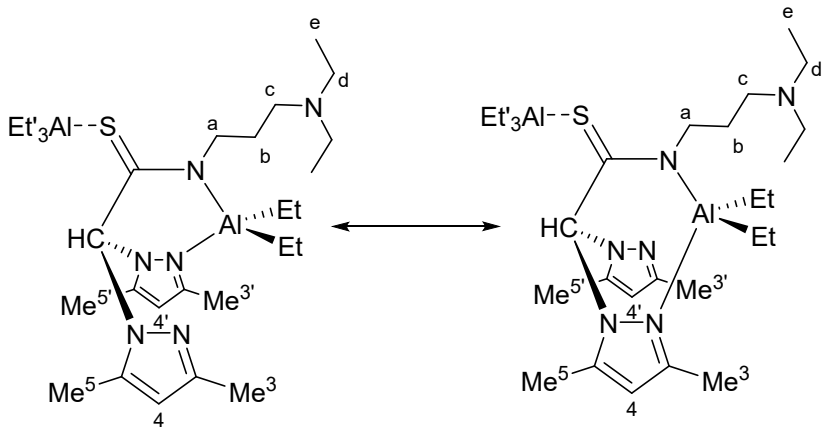


Figure S3. Variable temperature ^{1}H NMR spectra in the region from 6.3 to 3.3 ppm for compound **27** in toluene-d_8



(**27**)

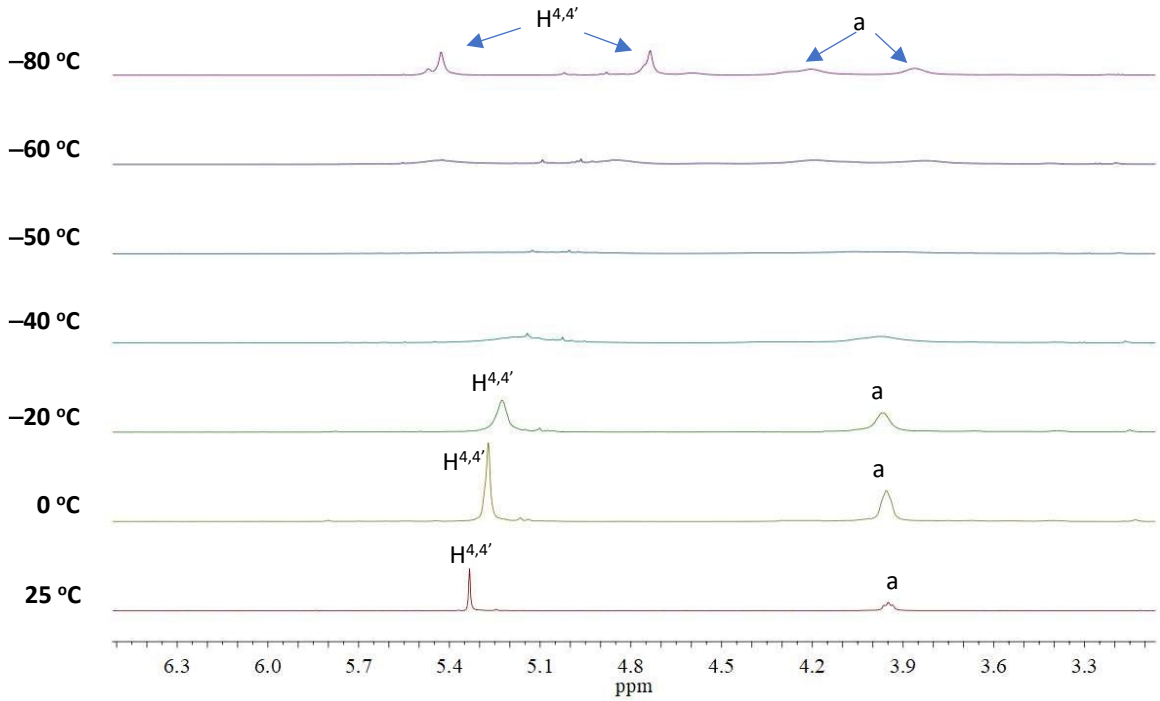


Table S1. Crystallographic data for complexes **17** and **22**

	17	**22**
Empirical formula	$C_{36}\ H_{64}\ Al_3\ N_5\ O$	$C_{27}H_{45}Al_2N_5O$
Formula weight	663.86	509.64
Temperature (K)	120(2)	290(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C c*	P 2_1/n
a(Å)	20.2041(8)	11.7654(13)
b(Å)	10.0613(7)	19.445(2)
c(Å)	20.8767(11)	13.2565(15)
α(°)	90	90
β(°)	115.022(3)	97.2330(10)
γ(°)	90	90
Volume(Å^3)	3845.5(4)	3008.7(6)
Z	4	4
Density (calculated) (g/cm^3)	1.147	1.125
Absorption coefficient (mm^{-1})	0.132	0.123
F(000)	1448	1104
Crystal size (mm^3)	0.17 x 0.17 x 0.12	0.42 x 0.39 x 0.26
Index ranges	$-20 \le h \le 20$ $-10 \le k \le 10$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-20 \le k \le 17$ $-14 \le l \le 14$
Reflections collected	9512	15843
Independent reflections	3824 [R(int) = 0.050]	3933 [R(int) = 0.0333]
Data / restraints / parameters	3824 / 2 / 417	3933 / 0 / 325
Goodness-of-fit on F^2	1.032	1.011
Final R indices [$I>2\sigma(I)$]	R1 = 0.0399 wR2 = 0.0932	R1 = 0.0391 wR2 = 0.0950
Largest diff. peak / hole	0.213 / -0.202	0.156 / -0.173

Table S2. Selected bond distances (Å) and angles (º) for complexes **17** and **22**

17		**22**	
Bond lengths (Å)			
Al(1)-N(5)	1.914(5)	Al(1)-N(5)	1.943(2)
Al(1)-C(13)	1.959(7)	Al(1)-N(1)	1.951(2)
Al(1)-C(15)	1.983(7)	Al(2)-O(1)	1.877(2)
Al(1)-N(1)	1.984(5)	N(2)-C(11)	1.440(3)
Al(2)-O(1)	1.868(4)	N(5)-C(12)	1.299(3)
Al(2)-C(19)	1.950(7)	N(5)-C(13)	1.515(3)
Al(2)-N(4)	1.958(5)	O(1)-C(12)	1.279(2)
Al(2)-C(17)	1.960(7)	C(11)-C(12)	1.537(3)
Al(3)-C(25)	1.984(7)		
Al(3)-C(21)	1.992(6)		
Al(3)-C(23)	1.992(7)		
Al(3)-O(1)	1.995(4)		
Angles (º)			
N(5)-Al(1)-C(13)	115.4(3)	N(5)-Al(1)-N(1)	96.69(8)
N(5)-Al(1)-C(15)	117.4(3)	N(5)-Al(1)-C(24)	119.8(2)
C(13)-Al(1)-C(15)	113.8(3)	C(24)-Al(1)-N(1)	108.7(1)
N(5)-Al(1)-N(1)	92.8(2)	N(5)-Al(1)-C(23)	107.0(1)
C(13)-Al(1)-N(1)	103.9(3)	C(24)-Al(1)-C(23)	118.9(1)
O(1)-Al(2)- C(19)	111.5(2)	N(1)-Al(1)-C(23)	101.9(1)
O(1)-Al(2)-N(4)	91.8(2)	O(1)-Al(2)-C(26)	104.6(1)
C(19)-Al(2)-N(4)	113.1(3)	O(1)-Al(2)-C(25)	102.2(1)
O(1)-Al(2)-C(17)	116.6(2)	C(26)-Al(2)-C(25)	115.4(2)
C(19)-Al(2)- C(17)	116.3(3)	O(1)-Al(2)-C(27)	105.9(1)
C(25)-Al(3)-C(21)	108.0(3)	C(26)-Al(2)-C(27)	112.1(1)
C(25)-Al(3)-O(1)	112.7(2)	C(25)-Al(2)-C(27)	115.0(1)
C(21)- Al(3)-O(1)	102.5(2)	O(1)-Al(2)-C(26)	104.7(1)
C(23)-Al(3)-O(1)	104.2(3)	C(12)-N(5)-C(13)	118.6(2)
C(25)- Al(3)-C(23)	112.9(3)	C(12)-N(5)-Al(1)	122.6(1)
		C(13)-N(5)-Al(1)	117.6(1)
		N(2)-C(11)-N(4)	111.7(2)
		N(2)-C(11)-C(12)	116.1(2)
		N(4)-C(11)-C(12)	108.3(2)
		O(1)-C(12)-N(5)	126.1(2)
		O(1)-C(12)-C(11)	112.6(2)
		N(5)-C(12)-C(11)	120.7(2)

General procedures for cyclic carbonates synthesis

General procedure for synthesis of cyclic carbonates at one bar pressure

An epoxide **28a–l** (1.7 mmol), complex **16** (19.2 mg, 34.0 μmol) and Bu_4NBr (10.7 mg, 33.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred for 24 h at 25 °C for epoxides **28a–j** or 50 °C for epoxides **28k,l**. The conversion of epoxide into cyclic carbonate was then determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane-EtOAc (9:1), then hexane-EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **29a**–**l** are all known compounds and the spectroscopic data for samples prepared using complex **16** were consistent with those reported in the literature.[1]

General procedure for synthesis of cyclic carbonates at 10 bar pressure

An epoxide **30a**–**d** (1.7 mmol), complex **16** (48.1 mg, 85.0 μmol) and Bu_4NBr (27.4 mg, 85.0 μmol) were placed in a stainless-steel pressure reactor with a magnetic stirrer bar. The reactor was pressurised to 10 bar of carbon dioxide and the reaction mixture was stirred at 25–90 °C for 24 h. Then the conversion of epoxide **30a**–**d** into cyclic carbonate **31a**–**d** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give a mixture of cyclic carbonate and unreacted epoxide. The mixture was purified by flash chromatography using a solvent system of first hexane, then hexane-EtOAc (9:1), then hexane-EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **31a**–**d** are all known compounds and the spectroscopic data for samples prepared using complex **16** were consistent with those reported in the literature.[1]

Figure S4. NMR Spectra for 1,2-hexylene carbonate **29a** in $CDCl_3$

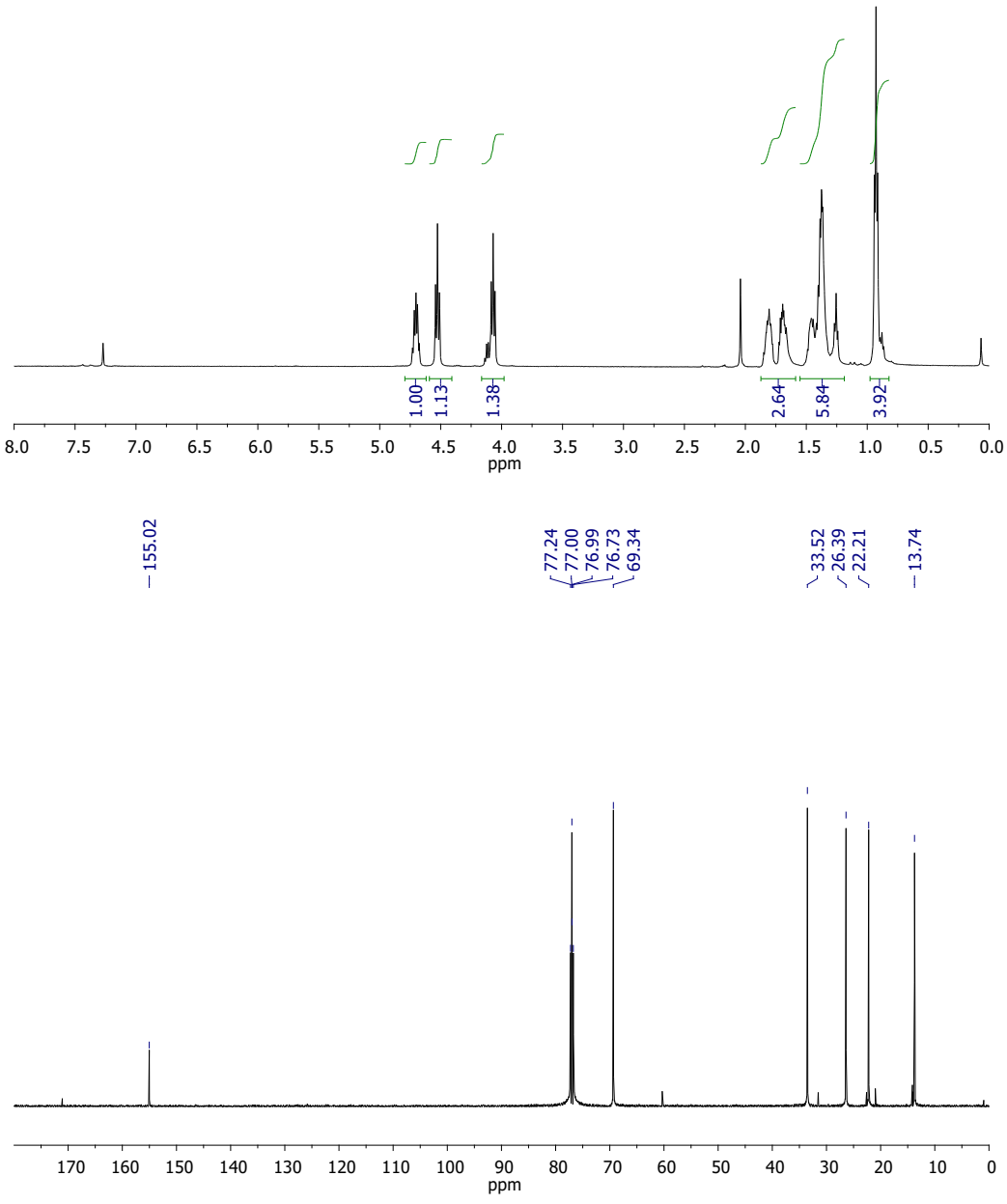


Figure S5. NMR Spectra for propylene carbonate **29b** in $CDCl_3$

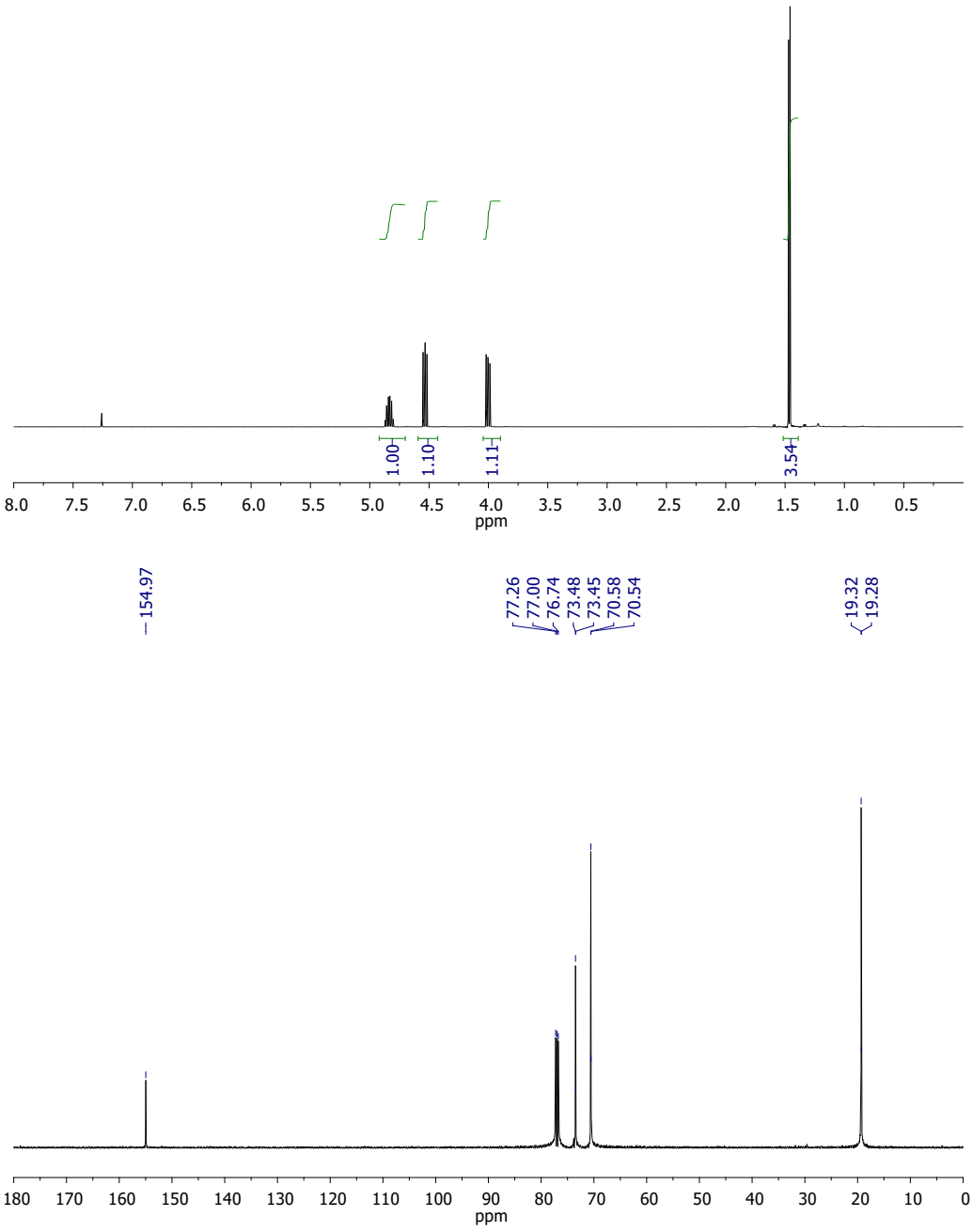


Figure S6. NMR Spectra for 1,2-decylene carbonate **29c** in $CDCl_3$

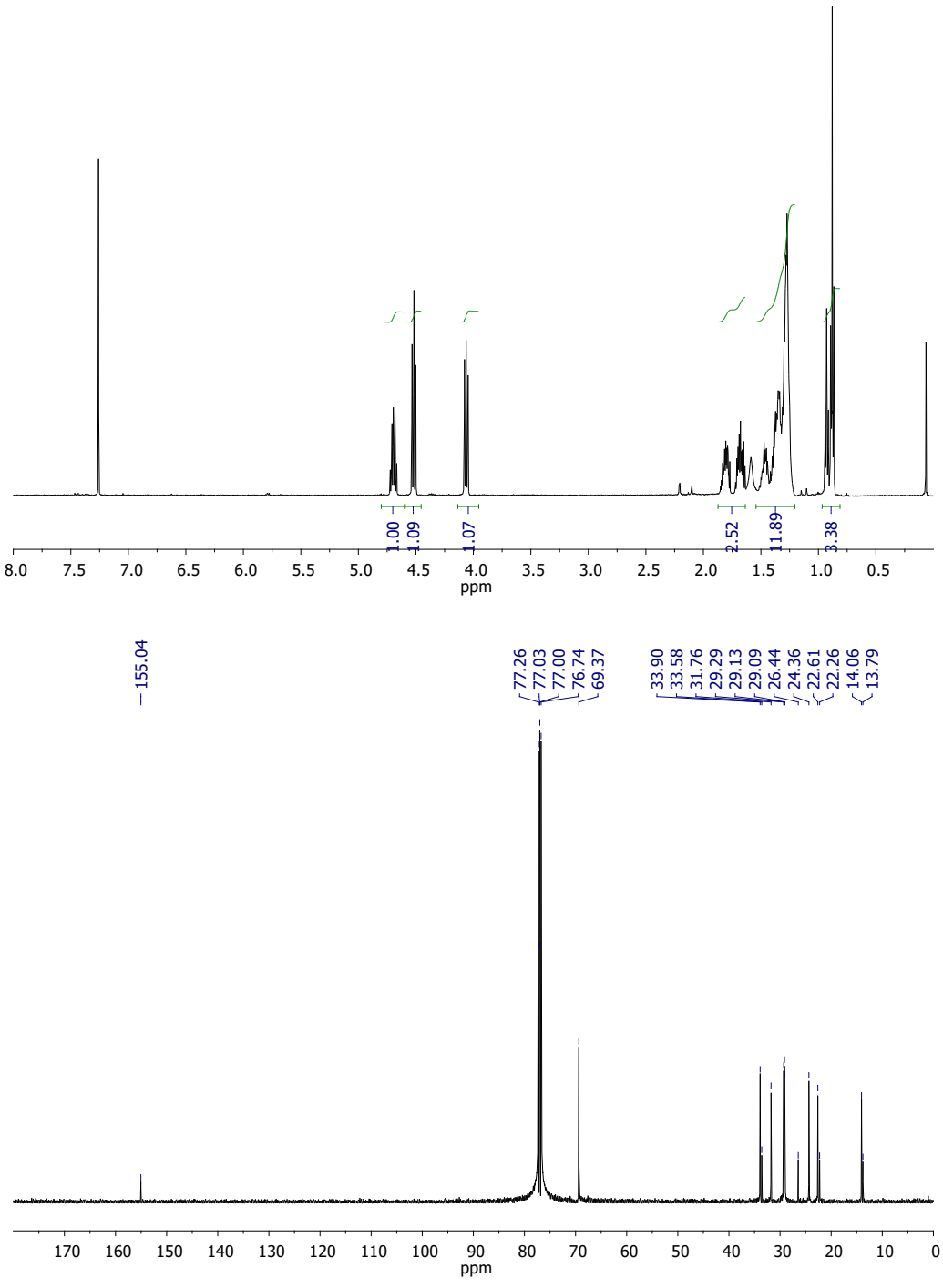


Figure S7. NMR Spectra for 1,2-dodecylene carbonate **29d** in $CDCl_3$

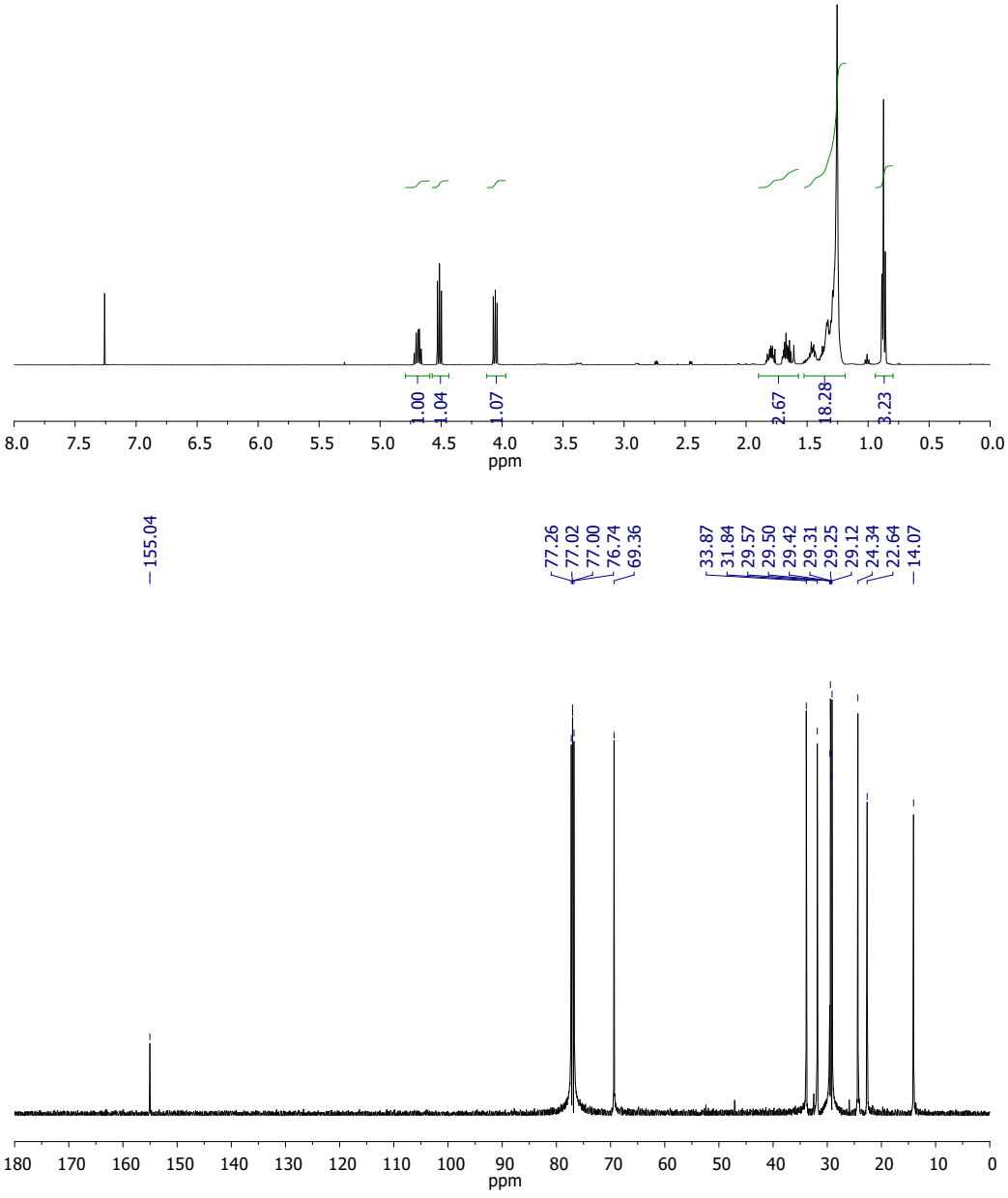


Figure S8. NMR Spectra for glycerol carbonate **29e** in DMSO-d_6

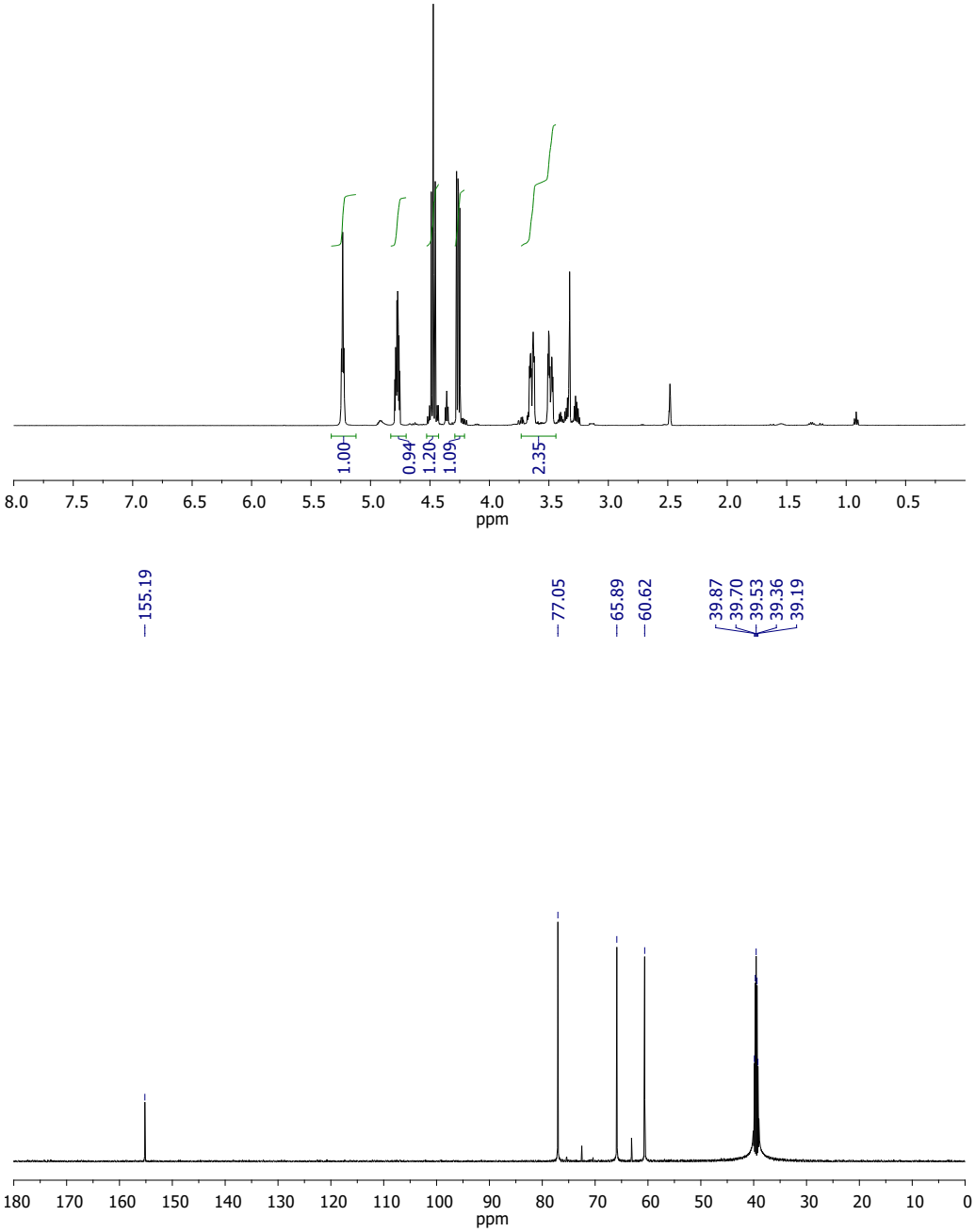


Figure S9. NMR Spectra for 3-chloropropylene carbonate **29f** in $CDCl_3$

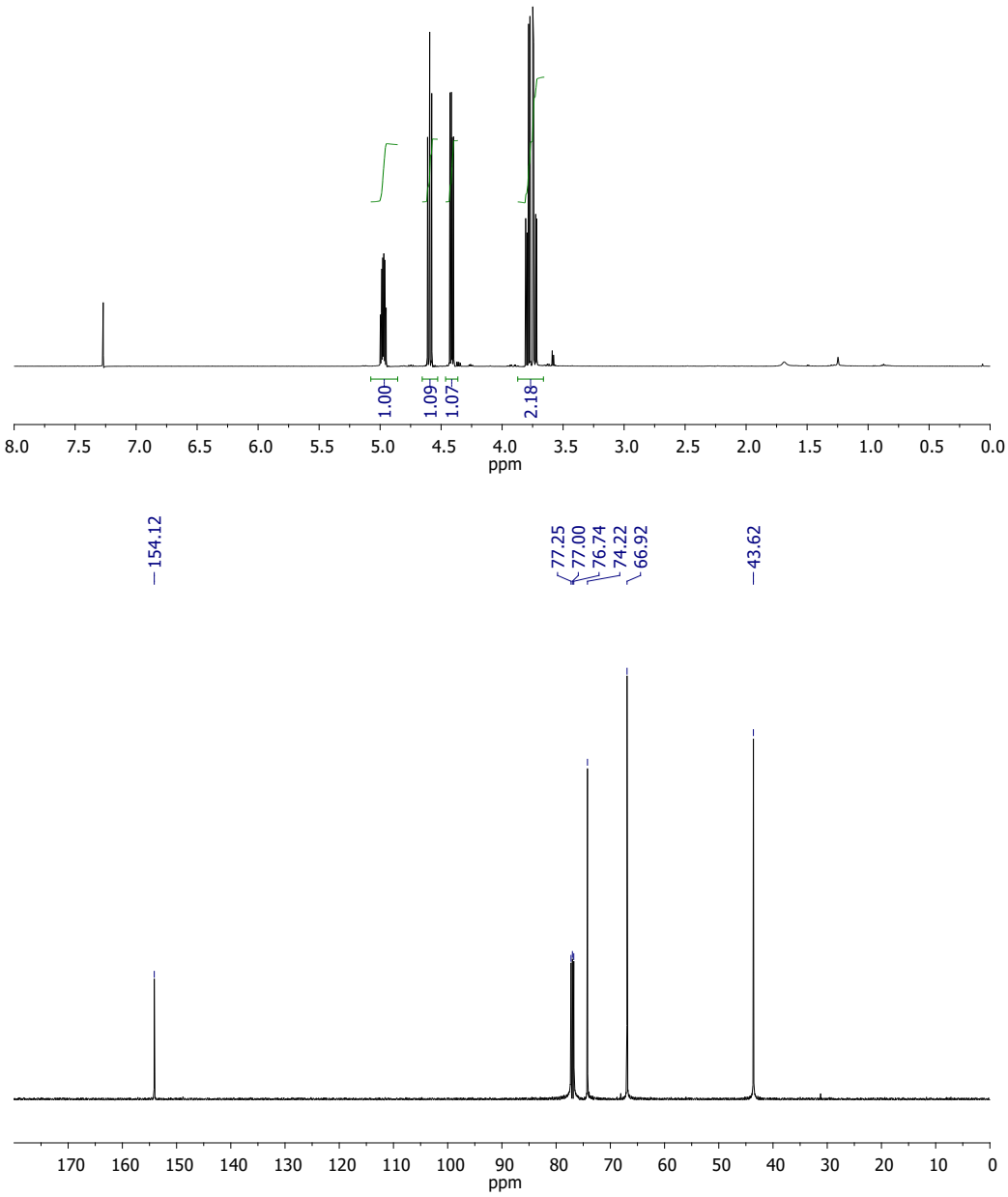


Figure S10. NMR Spectra for 3-phenoxypropylene carbonate **29g** in $CDCl_3$

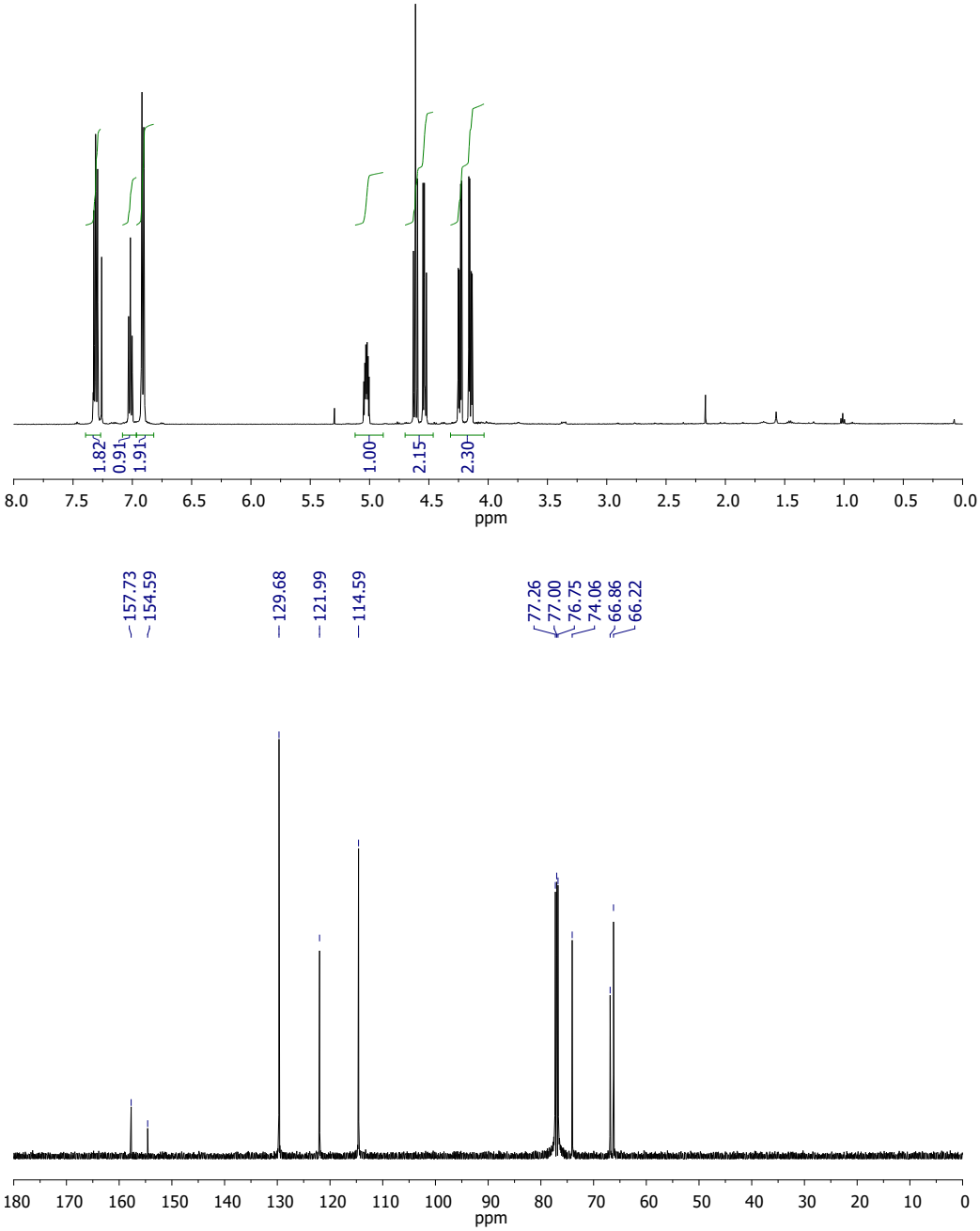


Figure S11. NMR Spectra for 3-propargyloxypropylene carbonate **29h** in $CDCl_3$

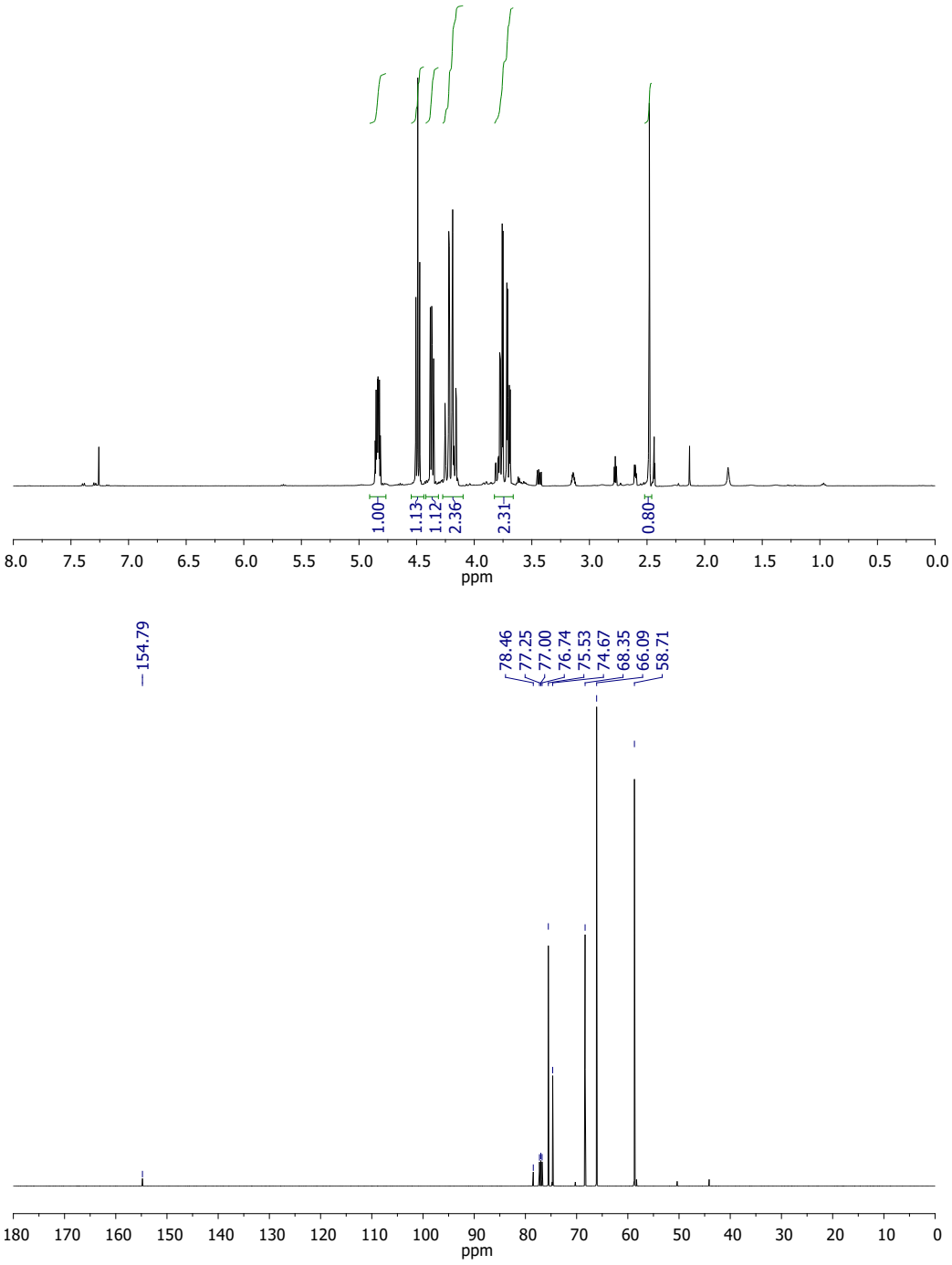


Figure S12. NMR Spectra for 3-vinyloxypropylene carbonate **29i** in $CDCl_3$

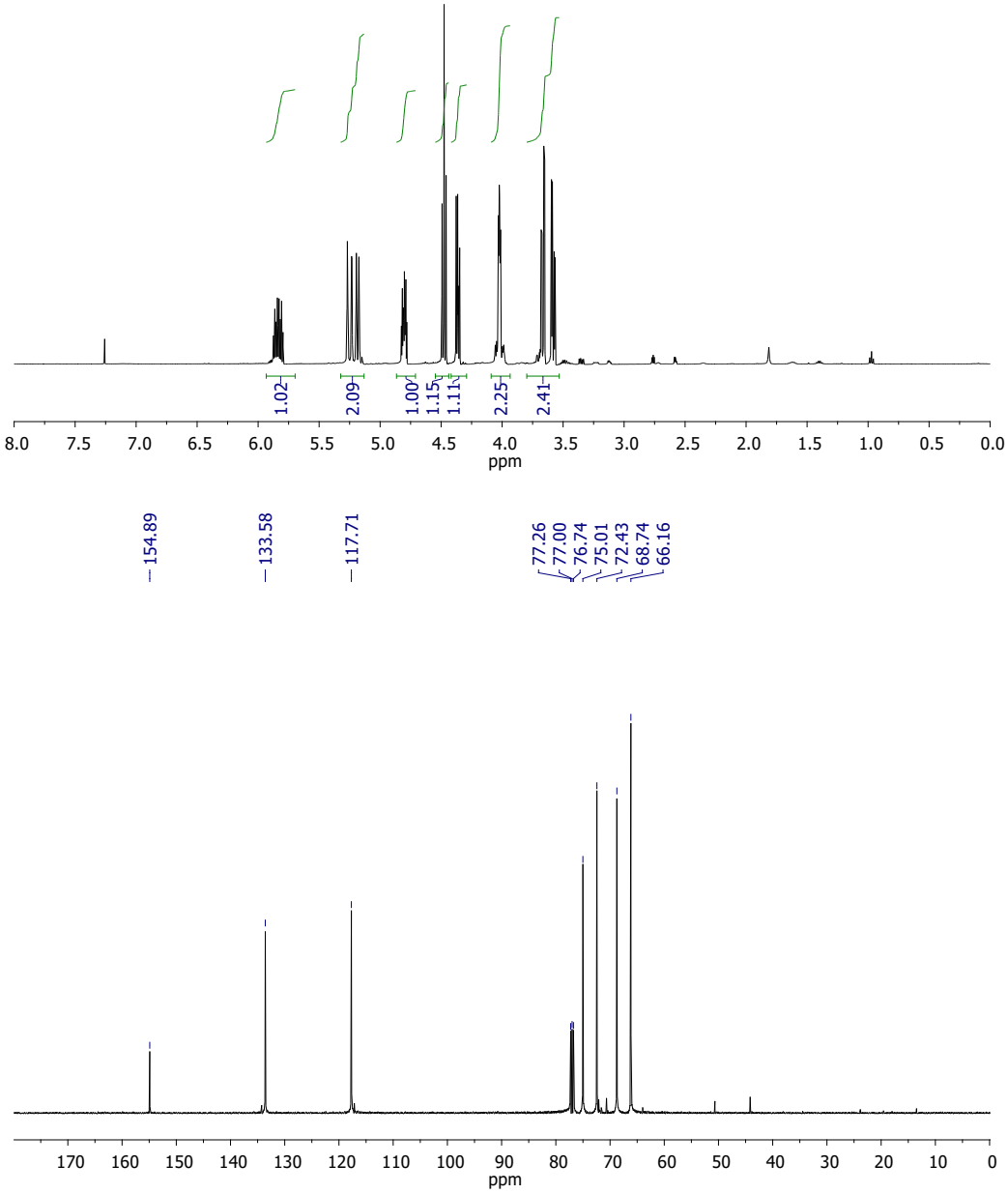


Figure S13. NMR Spectra for styrene carbonate **29j** in $CDCl_3$

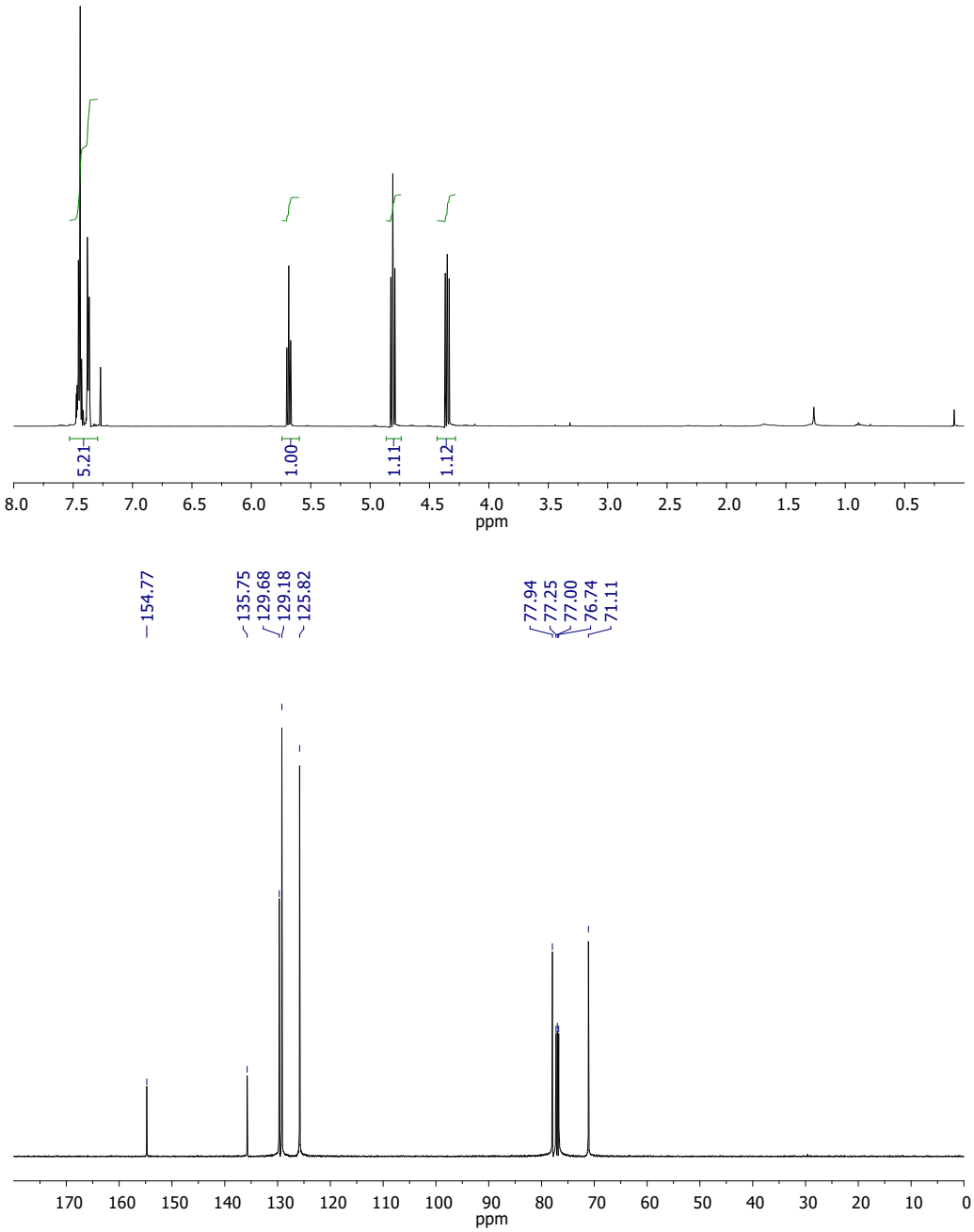


Figure S14. NMR Spectra for 4-chlorostyrene carbonate **29k** in $CDCl_3$

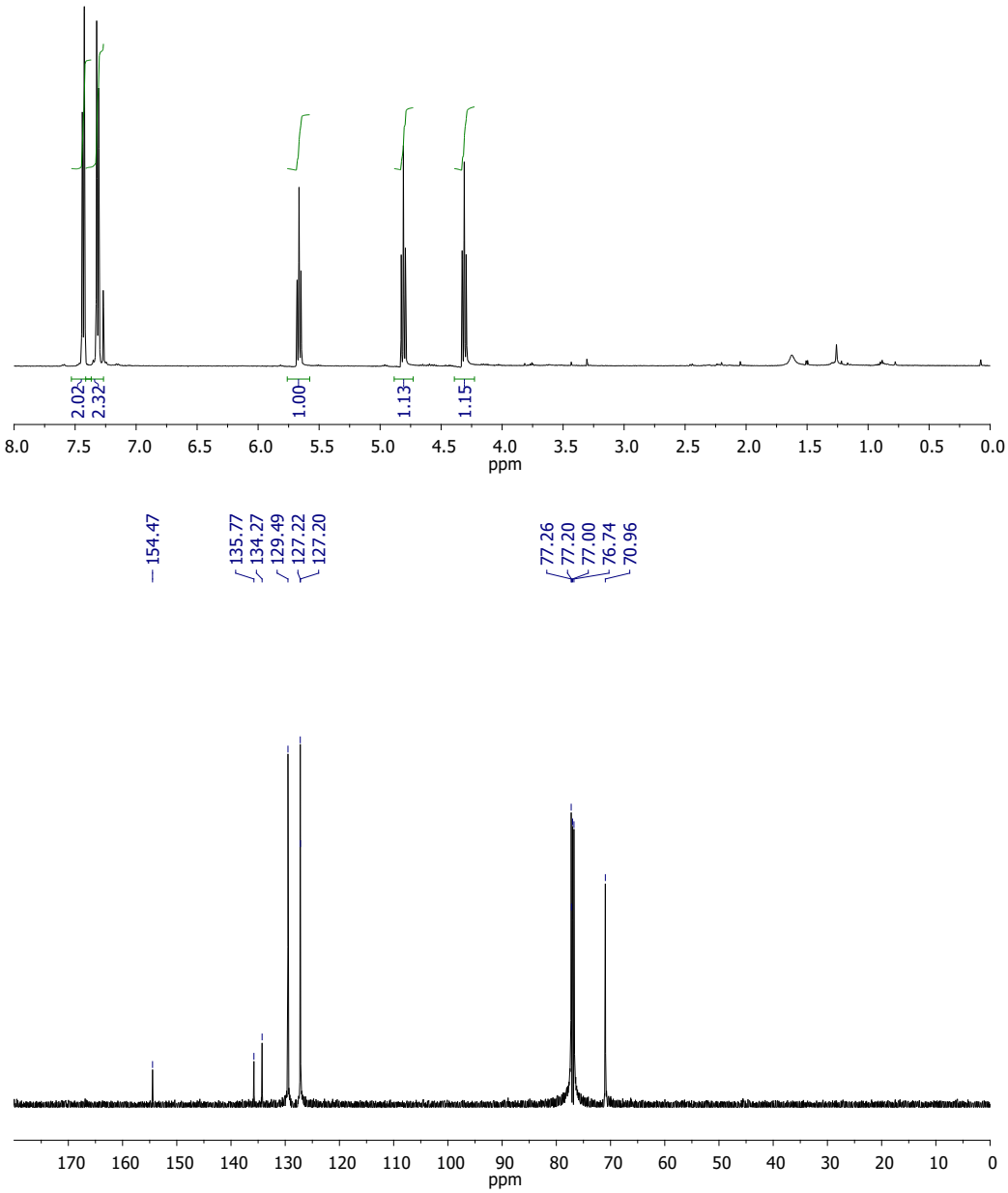


Figure S15. NMR Spectra for 4-bromostyrene carbonate **29l** in $CDCl_3$

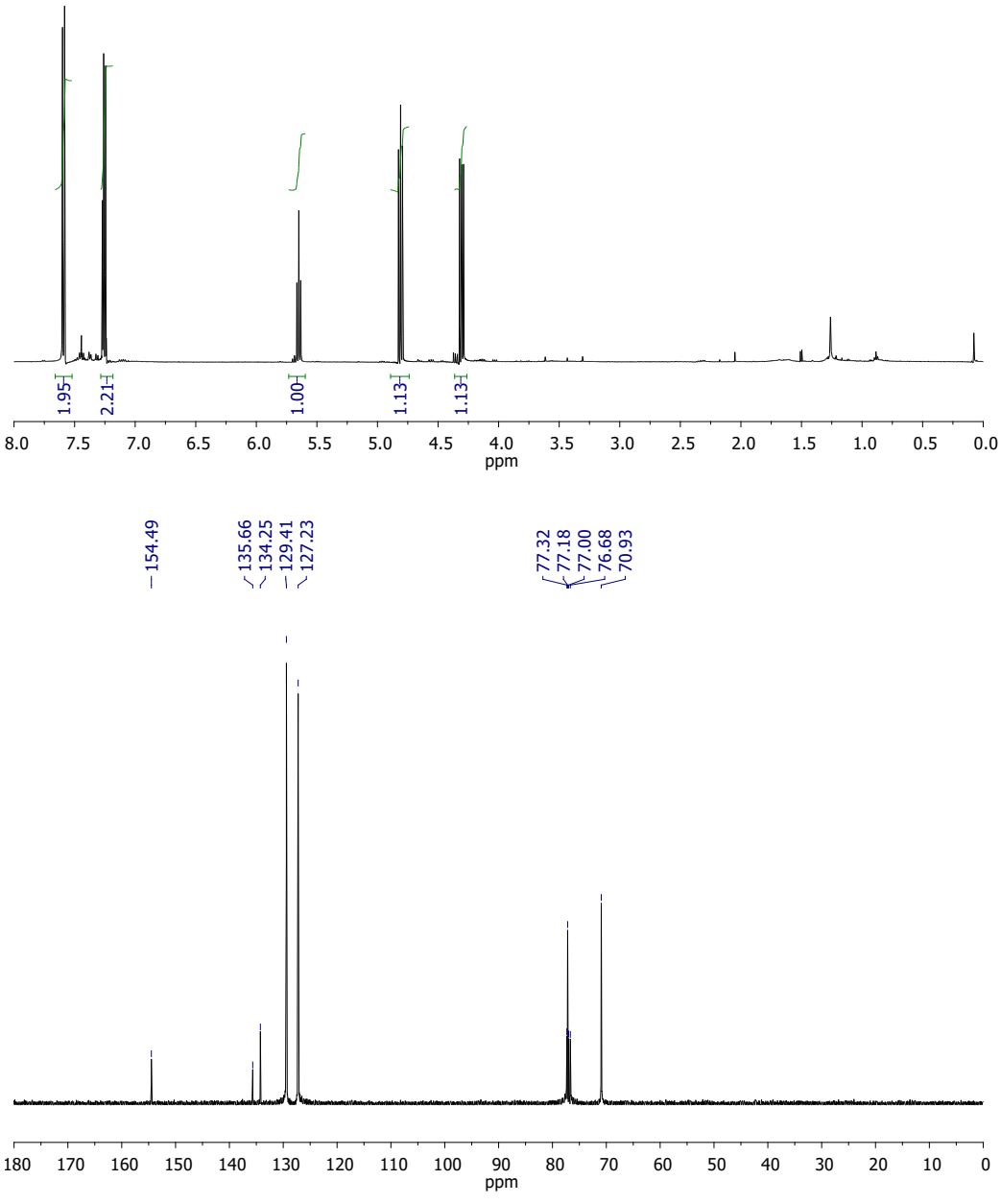


Figure S16. NMR Spectra for *cis*-cyclohexene carbonate **31a** in $CDCl_3$

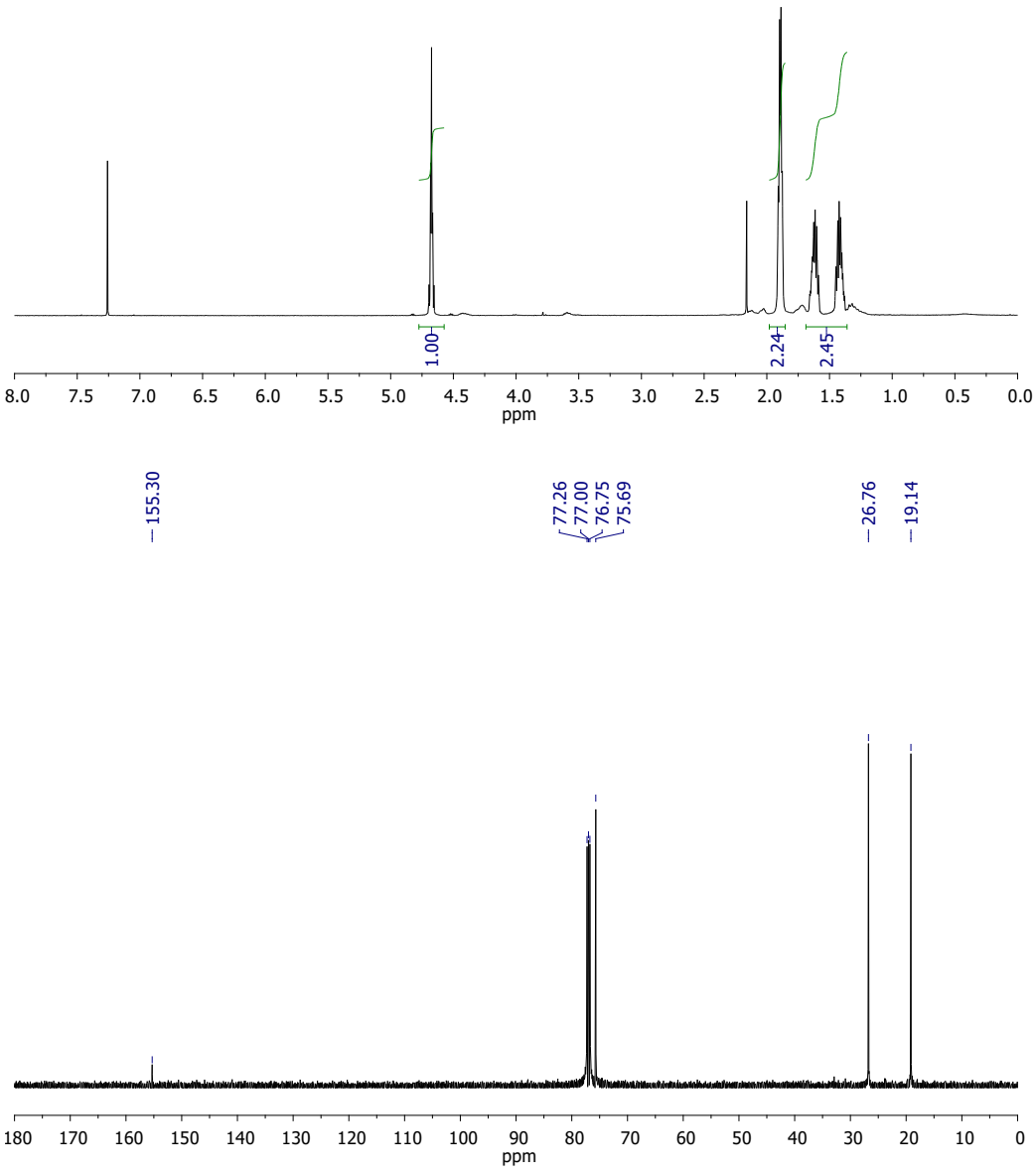


Figure S17. NMR Spectra for *cis*-cyclopentene carbonate **31b** in $CDCl_3$

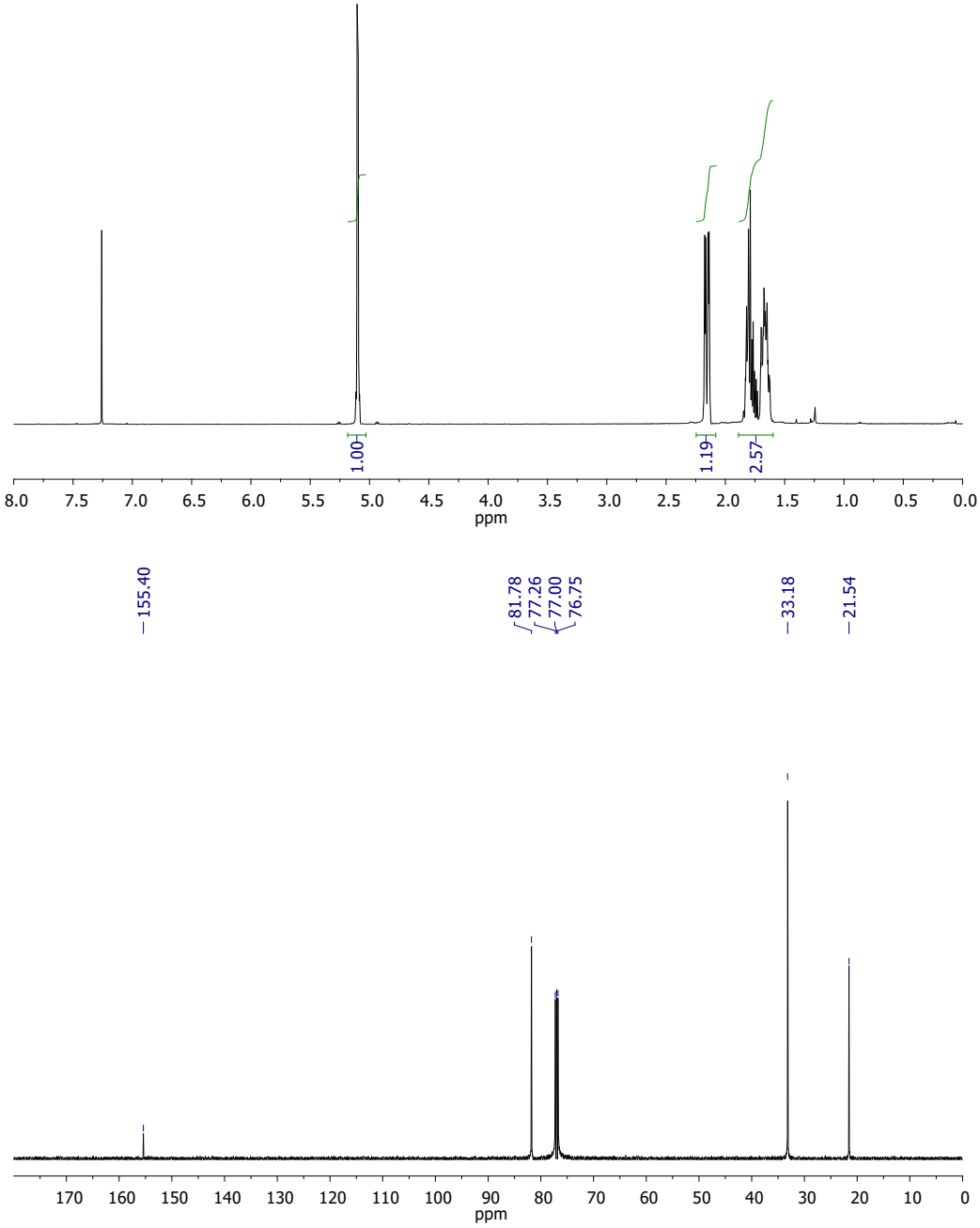


Figure S18. NMR Spectra for *trans*-1-phenyl-2-methylethylene carbonate **31c** in $CDCl_3$

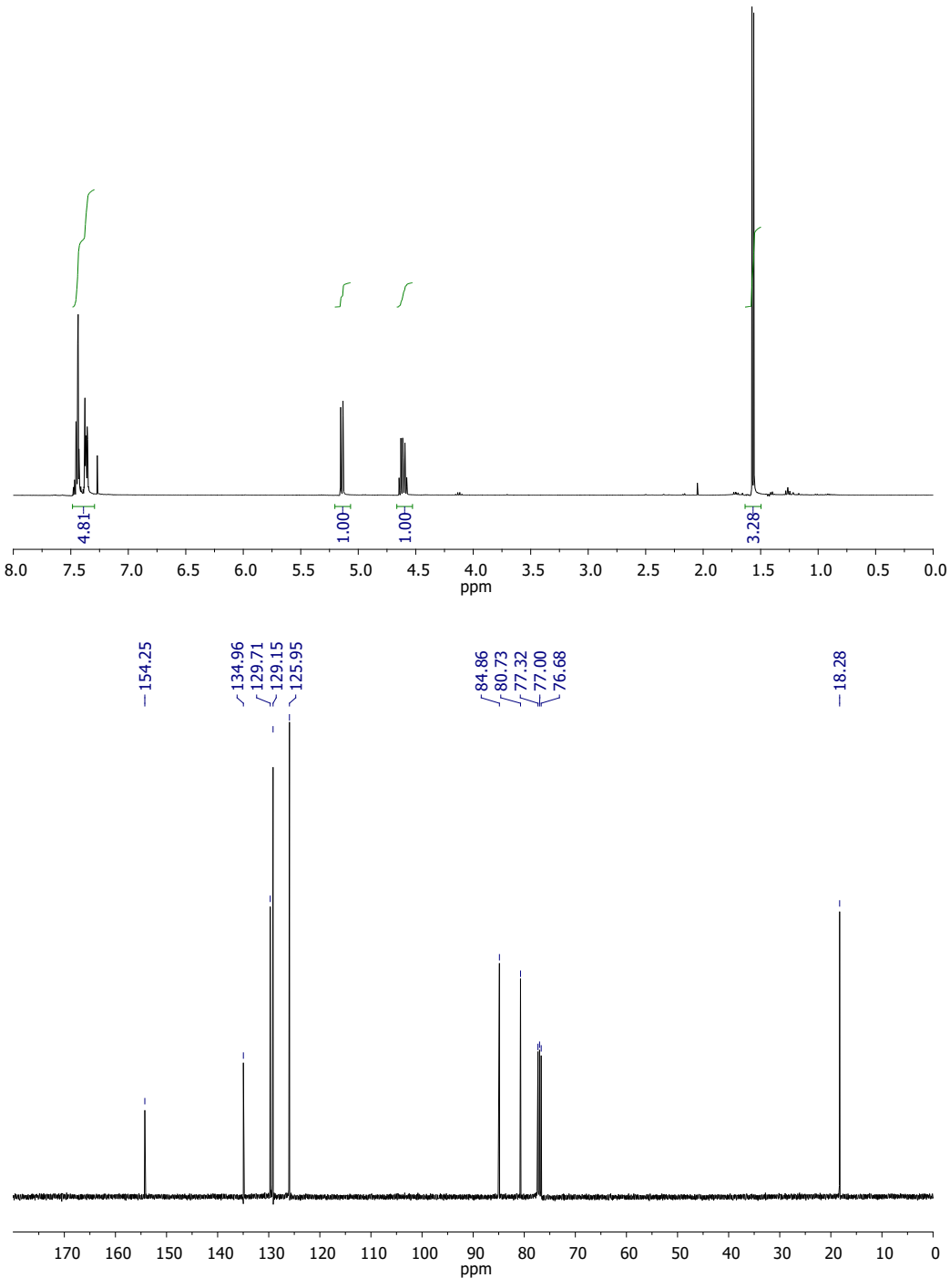
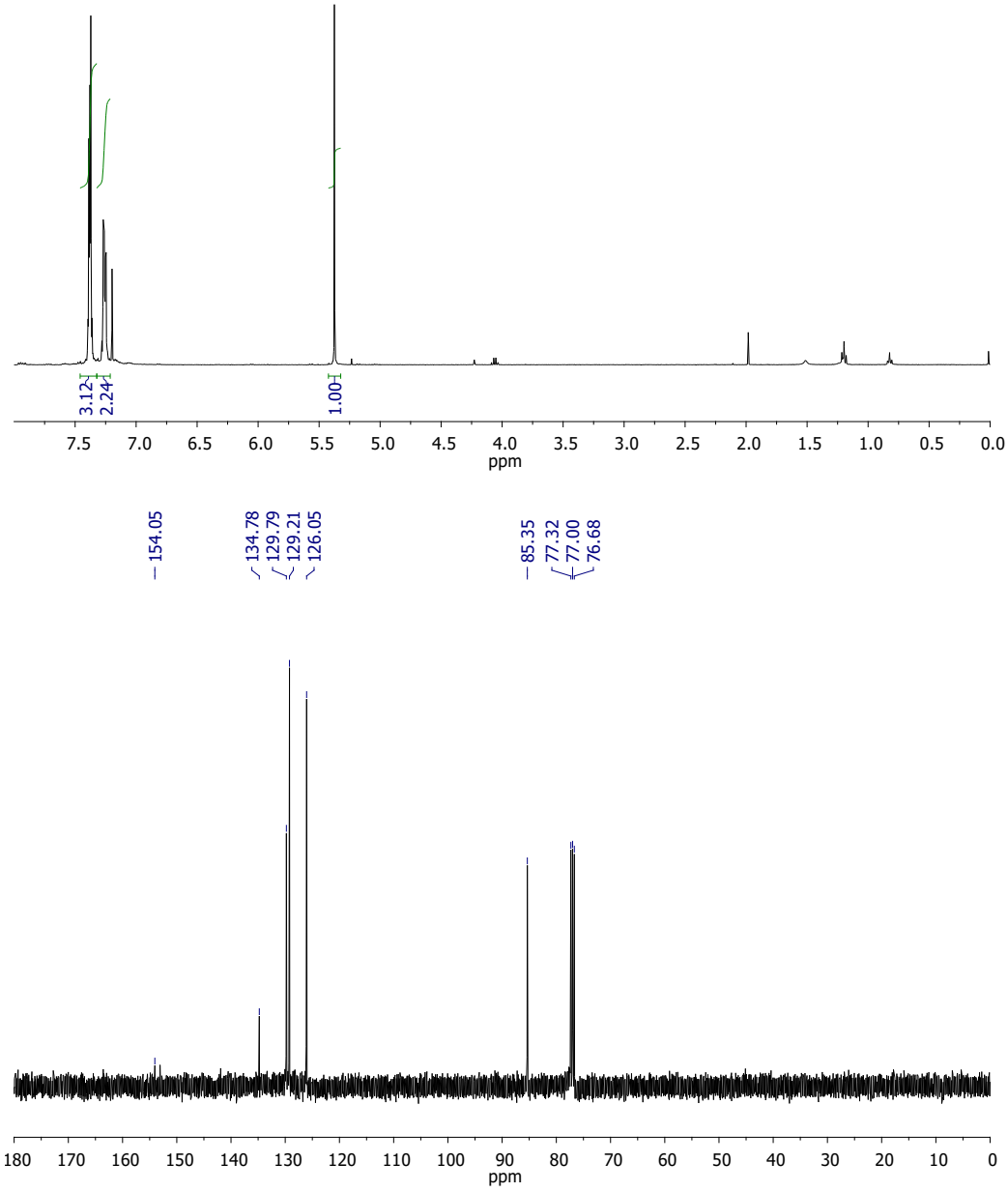


Figure S19. NMR Spectra for *trans*-1,2-diphenylethylene carbonate **31d** in $CDCl_3$



References

(1) (a) Castro-Osma, J. A.; Alonso-Moreno, C.; Lara-Sánchez, A.; Martínez, J.; North, M.; Otero, A., *Catal. Sci. Technol.*, **2014**, *4*, 1674; (b) Martínez, J.; Castro-Osma, J. A.; Earlam, A.; Alonso-Moreno, C.; Otero, A.; Lara-Sánchez, A.; North, M.; Rodríguez-Diéguez, A., *Chem. Eur. J.*, **2015**, *21*, 9850; (c) Martínez, J.; Castro-Osma, J. A.; Alonso-Moreno, C.; Rodríguez-Diéguez, A.; North, M.; Otero, A.; Lara-Sánchez, A., *ChemSusChem*, **2017**, *10*, 1175; (d) Meléndez, D. O.; Lara-Sánchez, A.; Martínez, J.; Wu, X.; Otero, A.; Castro-Osma, J. A.; North, M.; Rojas, R. S., *ChemCatChem*, **2018**, *10*, 2271; (e) de La Cruz-Martínez, F.; Martínez, J.; Gaona, M. A.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Rodríguez, A. M.; Castro-Osma, J. A.; Otero, A.; Lara-Sánchez, A., *ACS Sustain. Chem. Eng.*, **2018**, *6*, 5322.